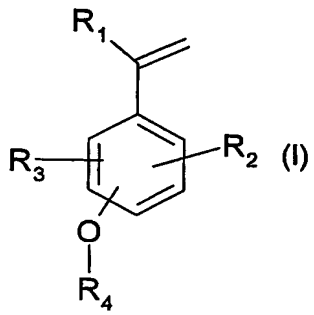
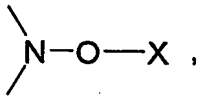
Claims

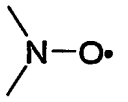
1. A process for the preparation of a narrow molecular weight distributed hydroxy-vinyl aromatic oligomer, cooligomer, polymer or copolymer with a polydispersity M_w/M_n between 1 and 2, which process comprises the steps reacting a composition
of at least one monomer of formula I

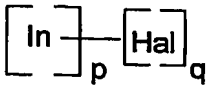


(I)

wherein
R_1 is H or CH_3;
R_2 and R_3 are independently hydrogen, C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkoxycarbonyl, C_1-C_8alkylthio, C_1-C_8dialkylamino, trihalogenmethyl;
R_4 is C_1-C_{12}alkyl or benzyl which is unsubstituted or substituted with one or two C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkoxycarbonyl, C_1-C_8alkylthio, C_1-C_8dialkylamino, trihalogenmethyl, halogen; or R_4 is a group phenyl(methyl)CH-, $(phenyl)_2CH$-, C_1-C_{12}alkyl-O-C(O)-, phenyl-CH_2-O-C(O)- or $(phenyl)_2CH$-O-C(O)-;

a1) in the presence of at least one nitroxylether having the structural element  , wherein X represents a group having at least one carbon atom and is such that the free radical X• derived from X is capable of initiating polymerization of ethylenically unsaturated monomers; or

a2) in the presence of at least one stable free nitroxyl radical  and a free radical initiator; or

a3) in the presence of a compound of formula (III)  (III) and a catalytically effective amount

of an oxidizable transition metal complex catalyst, wherein

p represents a number greater than zero and defines the number of initiator fragments;

q represents a number greater than zero;

[In] represents a radically transferable atom or group capable of initiating polymerization and

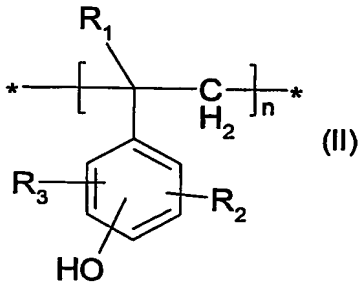
-[Hal] represents a leaving group; or

a4) in an anionic polymerization reaction in the presence of a metal or organo metal catalyst;

and optionally simultaneously or in a subsequent step with one or more ethylenically unsaturated monomers different from those of formula (I);

and

b) isolating the resulting polymer and subjecting it to a reaction with a halosilane giving a polymer with repeating units of formula II



(II)

and with a degree of OH-groups of between 10 mol % and 100 mol %, based on the molar amount of protected hydroxy-vinyl aromatic monomer of formula I.

2. A process according to claim 1 wherein halosilane is iodosilane.

3. A process according to claim 1 wherein the polymerization is carried out according to steps a1) or a2).

4. A process according to claim 1 wherein in formula I

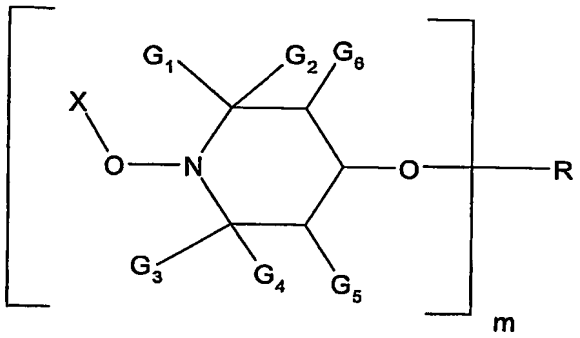
R_1 is H;

R_2 and R_3 are H;

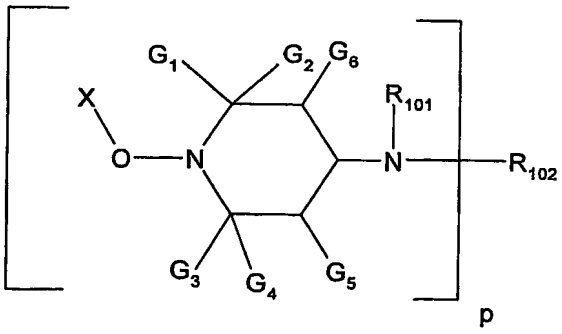
OR_4 is in the 4-position and

R_4 is C_1-C_4alkyl, benzyl, C_1-C_4alkoxycarbonyl or benzyloxycarbonyl.

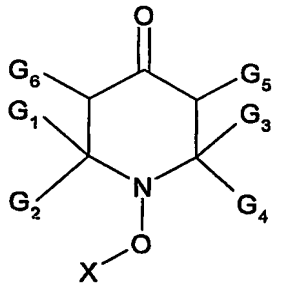
5. A process according to claim 1, wherein the nitroxylether in step a1) is of formula A, B or O,



(A) ,



(B) ,



(O)

wherein

m is 1,

R is hydrogen, C_1-C_{18}alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

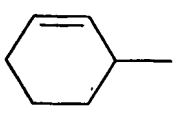
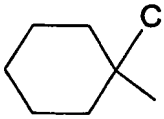
R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl,

G_1 and G_3 are methyl and G_2 and G_4 are ethyl or propyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl or propyl; and

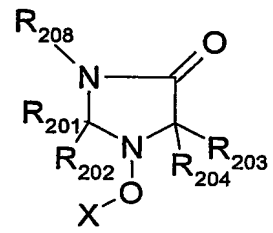
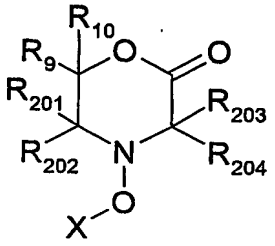
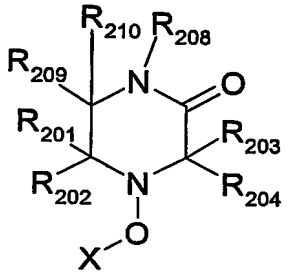
X is selected from the group consisting of

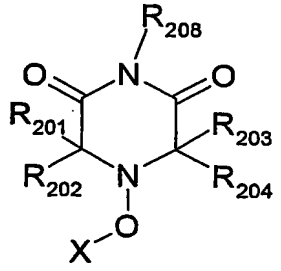
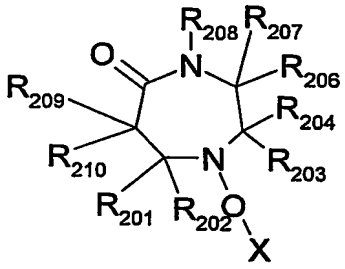
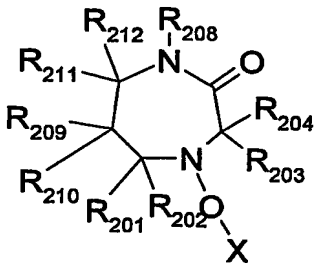
$-CH_2$-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, $(C_5$-C_6cycloalkyl$)_2CCN$, $(CH_3)_2CCN$,

 ,  , $-CH_2CH=CH_2$, $CH_3CH-CH=CH_2$ $(C_1$-C_4alkyl$)CR_{20}$-C(O)-phenyl, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-$(C_1$-$C_4)$alkoxy, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-$(C_1$-$C_4)$alkyl, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-N-di$(C_1$-$C_4)$alkyl, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-NH$(C_1$-$C_4)$alkyl, $(C_1$-$C_4)$alkyl-CR_{20}-C(O)-NH_2, wherein

R_{20} is hydrogen or $(C_1$-$C_4)$alkyl.

6. A process according to claim 1, wherein the nitroxylether of step a1) is of formula (Ic), (Id), (Ie), (If), (Ig) or (Ih)


(Ic),

(Id),

(Ie),


(If),

(Ig),

(Ih),

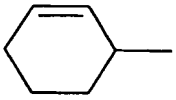
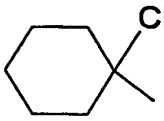
wherein R_{201}, R_{202}, R_{203} and R_{204} independently of each other are C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by OH, halogen or a group $-O-C(O)-R_{205}$, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205}

group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl or R_{201} and R_{202} and/or R_{203} and R_{204} together with the linking carbon atom form a C_3-C_{12}cycloalkyl radical;

R_{205}, R_{206} and R_{207} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

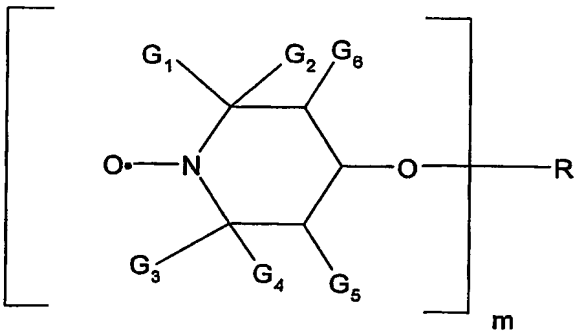
R_{208} is hydrogen, OH, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by one or more OH, halogen or a group -O-C(O)-R_{205}, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205} group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl, C_7-C_9phenylalkyl, C_5-C_{10}heteroaryl, -C(O)-C_1-C_{18}alkyl, -O-C_1-C_{18}alkyl or -COOC_1-C_{18}alkyl;

R_{209}, R_{210}, R_{211} and R_{212} are independently hydrogen, phenyl or C_1-C_{18}alkyl; and

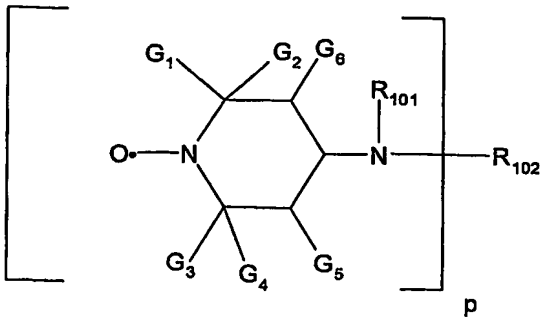
X is selected from the group consisting of -CH_2-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, (C_5-C_6cycloalkyl)$_2$CCN, $(CH_3)_2$CCN,  ,  , -$CH_2CH{=}CH_2$, CH_3CH-$CH{=}CH_2$ (C_1-C_4alkyl)CR_{20}-C(O)-phenyl, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkoxy, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-N-di(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH_2, wherein

R_{20} is hydrogen or (C_1-C_4)alkyl.

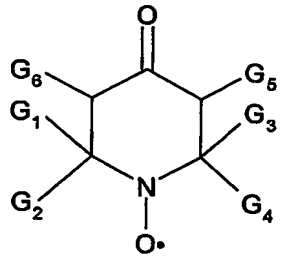
7. A process according to claim 1, wherein the nitroxyl radical of step a2) is of formula A', B' or O',



(A') ,



(B')



(O')

wherein

m is 1,

R is hydrogen, C_1-C_{18}alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

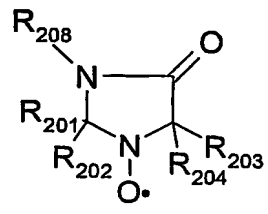
R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula $-CH_2CH(OH)-Z$ or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

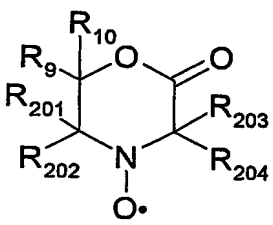
G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl, and

G_1 and G_3 are methyl and G_2 and G_4 are ethyl or propyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl or propyl.

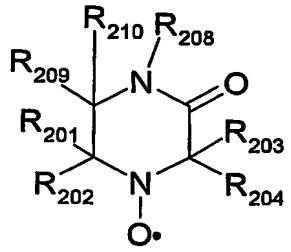
8. A process according to claim 1, wherein the nitroxyl radical of step a2) is of formula (Ic'), (Id'), (Ie'), (If'), (Ig') or (Ih')



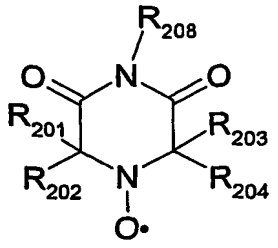
(I'c),



(I'd),



(I'e),



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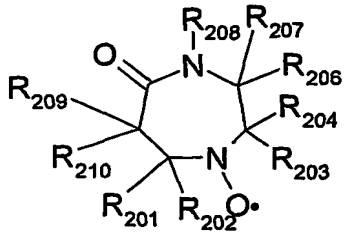
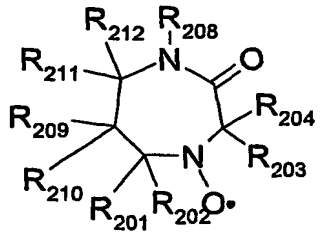


(I'g),



(I'h),

wherein R_{201}, R_{202}, R_{203} and R_{204} independently of each other are C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by OH, halogen or a group -O-C(O)-R_{205}, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205} group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl or R_{201} and R_{202} and/or R_{203} and R_{204} together with the linking carbon atom form a C_3-C_{12}cycloalkyl radical;

R_{205}, R_{206} and R_{207} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

R_{208} is hydrogen, OH, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by one or more OH, halogen or a group -O-C(O)-R_{205}, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205} group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl, C_7-C_9phenylalkyl, C_5-C_{10}heteroaryl, -C(O)-C_1-C_{18}alkyl, -O-C_1-C_{18}alkyl or -COOC_1-C_{18}alkyl; and

R_{209}, R_{210}, R_{211} and R_{212} are independently hydrogen, phenyl or C_1-C_{18}alkyl.

9. A process according to claim 1, wherein in step a3)

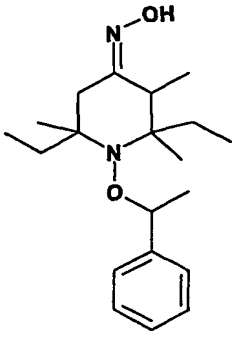
[In] represents the polymerization initiator fragment of a polymerization initiator of formula (III) capable of initiating polymerization of monomers or oligomers which polymerization initiator is selected from the group consisting of C_1-C_8-alkyl halides, C_6-C_{15}-aralkylhalides, C_2-C_8-haloalkyl esters, arene sulfonyl chlorides, haloalkanenitriles, α-haloacrylates and halolactones,

p and q represent one and the other components are as defined in claim 1.

10. A process according to claim 1, wherein in step a3) the oxidizable transition metal in the transition metal complex salt is present as a transition metal complex ion in the lower oxidation state of a redox system.

11. A process according to claim 10, wherein the transition metal complex ion is a Cu(I) complex ion in the Cu(I)/Cu(II) system.

12. A process according to claim 1 wherein the nitroxyl ether of formula



is used in the polymerization step a1).

13. A process according to claim 1 wherein the optionally used additional ethylenically unsaturated monomer is selected from the group consisting of an acrylic acid ester, acrylamide, acrylnitrile, methacrylic acid ester, methacrylamide, methacrylnitrile and styrene.

14. A process according to claim 1 wherein the polymerization temperature in the steps a1), a2) or a3) is between 90° C and 150° C.

15. A process according to claim 1 wherein the hydroxy-vinyl aromatic oligomer, cooligomer, polymer or copolymer has a weight molecular weight average from 2000 to 30 000 Daltons.

16. A process according to claim 1 wherein the iodosilane reagent of step b) is $R_{13}R_{14}R_{15}SiI$, wherein R_{13}, R_{14} and R_{15} are independently C_1-C_8alkyl, chloromethyl, vinyl or phenyl.

17. A process according to claim 1 wherein the reaction with a halosilane reagent is carried out using a chlorosilane reagent from $R_{13}R_{14}R_{15}SiCl$ wherein R_{13}, R_{14} and R_{15} are independently C_1-C_8alkyl, chloromethyl, vinyl or phenyl in the presence of a halide salt and/or thiol, wherein the halide salt is selected from the group consisting of alkaline metal halide, alkaline-earth metal halide, ammonium halide or phosphonium halide.

18. A formulated photoresist prepared from a polymer obtainable by a process according to claim 1.